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(54) Vapour phase deposition process

(57) Vapour phase deposition of e.g. silica or germania is effected by irradiating a mixture of oxygen and the corresponding tetrachloride with light preferably from a CO_2 laser. The gas includes an inert molecule, e.g. sulphur hexafluoride, which absorbs the radiation and then transfers kinetic energy to the reactive gases and which has a spectral absorption band corresponding to the wavelength of the radiation.

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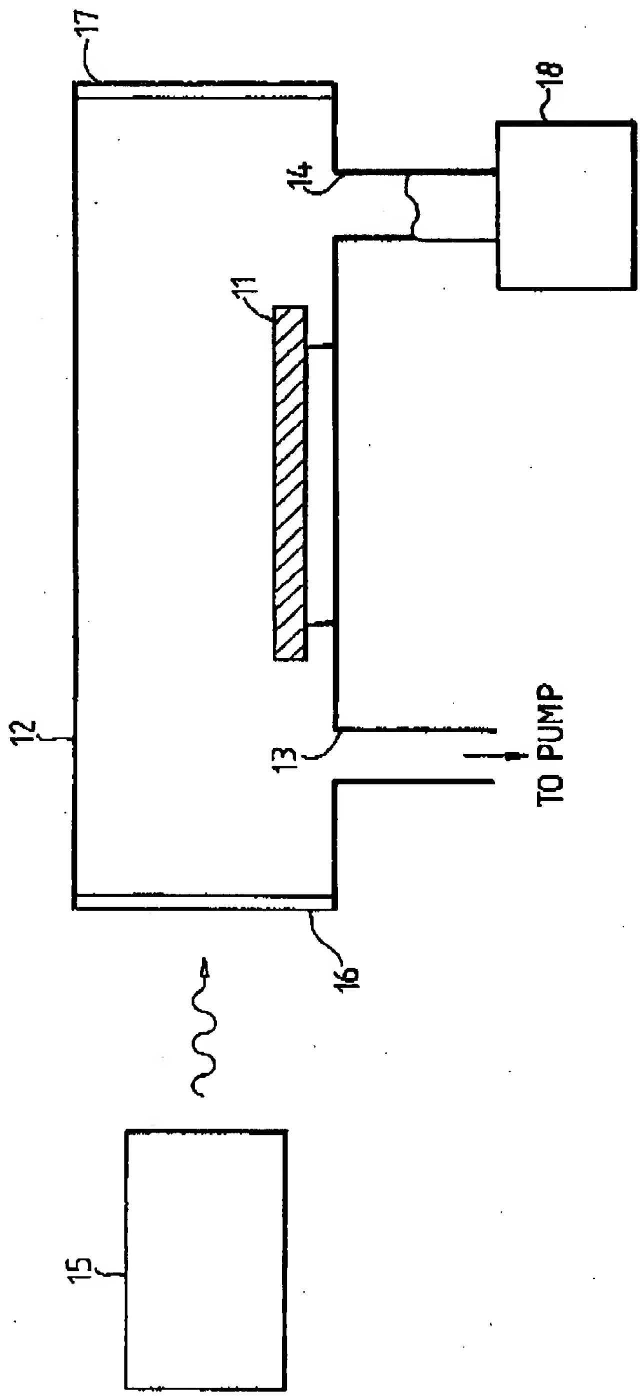

SPECIFICATION

Vapour phase deposition process

This invention relates to vapour deposition processes, e.g. for the production of optical fibre preforms.

High purity materials, e.g. oxides for glasses and ceramics, are conventionally produced by vapour deposition processes. A necessary feature of many of these processes is that the temperature of the vapour be raised to a point at which the deposition reaction can occur to form the desired material. Conventionally, a substrate to be provided with a surface coating is placed in a reactor vessel containing a suitable vapour. The assembly is heated to raise the vapour to a temperature at which the deposition process takes place. It will be appreciated that, in this process, the reactor vessel itself is heated. It has been found that, under such conditions, contaminant materials can evaporate from the surface of the reactor vessel thus limiting the obtainable purity of the deposited material. For very high purity applications, e.g. the manufacture of optical fibre preforms, this contamination can be significant.

In a typical process used in the production of optical fibre preforms a surface layer of silicon and/or germania is deposited on a substrate preform surface by thermal oxidation of the corresponding chloride(s). In one version of this process a glass preform tube comprises a reactor vessel, the inner walls of which provide a substrate surface on which deposition is effected. It has been found that the heating required to promote the conventional oxidation process can cause distortion of the tube, the phenomenon being known in the art as dog-legging. This limits both the length of the preform that can be treated and the time for which deposition is effected. The problem is particularly acute in the production of germania doped preforms where it is preferred to provide a preform of relatively low melting point to facilitate drawing down into fibre.

In an attempt to overcome this problem, it has been proposed to heat the reactant vapour whilst the containing reactor vessel remains relatively cool. A particularly promising technique is the laser initiation of chemical vapour deposition. In this process laser light is employed to provide the necessary energy to initiate reaction of the vapour constituents to effect deposition. If such a process is to be commercially viable it is necessary to employ an efficient laser. Of the available photon sources, the carbon dioxide laser is the most attractive for industrial applications. However the introduction of laser initiation to the manufacture of optical fibre preforms has been inhibited by the absence of light absorption by

The reactants commonly employed, e.g. oxygen, silicon tetrachloride and germanium tetrachloride, have no absorption bands corresponding to the light output of a carbon dioxide laser and it has not hereto been possible to deliver sufficient optical energy to such materials to initiate reaction.

The object of the present invention is to minimise or to overcome this disadvantage.

According to the invention there is provided a photon initiated chemical vapour deposition process, the process including exposing a reactant gas mixture to photon radiation, and incorporating, in said mixture, one or more materials having a spectral absorption band corresponding to the wavelength of the radiation whereby energy is absorbed from the radiation and transferred to the reactant gas to effect reaction and deposition.

As the active reactants are not required to have an absorption band in the particularly narrow region of the spectrum corresponding to the laser output the constraints on the nature of these reactants are removed.

An embodiment of the invention will now be described with reference to the accompanying drawing in which the single figure is a schematic diagram of a vapour deposition apparatus.

Referring to the drawing, chemical vapour deposition is performed on a substrate 11 mounted in a reactor vessel 12 having inlet and outlet ports, 13 and 14 respectively, for reactant gases and exhaust gases. The substrate 11 may comprise an optical fibre preform. Typically the reactant gas comprises oxygen together with silicon tetrachloride, germanium tetrachloride or mixtures thereof. Infra-red radiation is directed into the reactor 12 from a laser 15, e.g. a carbon dioxide laser having an output wavelength in the range 9 to 11 microns, via an input window 16. Non-absorbed radiation is emitted from the reactor vessel via an output window 17.

In use, the reactor vessel is evacuated via a pump 18 and is then filled with a reactant gas mixture from a supply 18. The gas mixture includes a constituent, typically inert, having a spectral absorption band corresponding to the output spectrum of the laser. For the purpose we prefer to employ sulphur hexafluoride or silicon tetrachfluoride. The function of the inert constituent is to catalyse the deposition reaction by absorbing energy from the laser radiation and transferring this energy to the reactants by molecular collisions. By this process the temperature of the reactant gas adjacent the substrate 11 is raised sufficiently from the deposition reaction to proceed.

The inert gas takes no chemical part in the reaction but remains unchanged. Thus, this material may be removed from the reaction products and recycled.

As the inert gas contributes to the heat

to employ small molecules with relatively few degrees of freedom. Typical of such molecules are sulphur hexafluoride, silicon tetrafluoride, boron trichloride and the lower fluorinated hydrocarbons.

In a further modification of the technique the substrate may be dispensed with and the reaction performed in the gas phase to effect powder formation. The power may be collected by fitration or by electrostatic precipitation.

Although the technique has been described with particular reference to optical fibre preforms, it is not so limited but may of course be used in other surface deposition or etching applications. It will also be appreciated that the technique may be used not only for silica and/or germania deposition but also for other oxides, doped oxides and mixed oxides as well as other non-oxide materials.

CLAIMS

1. A photon initiated chemical vapour deposition process, the process including exposing a reactant gas mixture to proton radiation, and incorporating, in said mixture, one or more materials having a spectral absorption band corresponding to the wavelength of the radiation whereby energy is absorbed from the radiation and transferred to the reactant gas to effect reaction and deposition.

2. A process as claimed in claim 1, wherein the radiation comprises infa-red radiation in the wavelength region 9 to 11 microns.

3. A process as claimed in claim 2, wherein the laser is a carbon dioxide laser.

4. A process as claimed in claim 1, 2 or 3, wherein the energy absorbing material comprises sulphur hexafluoride or silicon tetrafluoride.

5. A process as claimed in any one of claims 1 to 4, wherein the reactant gas comprises oxygen together with silicon tetrachloride, germanium tetrachloride or mixtures thereof.

6. A vapour deposition process substantially as described herein with reference to the accompanying drawings.

7. An optical fibre preform produced via a process as claimed in any one of claims 1 to 5.

8. An optical fibre drawn from a preform as claimed in claim 7.

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(21) Application number:	63240217	(71) Applicant:	VICTOR CO OF JAPAN LTD
(22) Date of filing:	26.09.1988	(72) Inventor:	KAWAGUCHI TOSHIHIKO

(54) LASER CVD DEVICE

(57) Abstract:

PURPOSE: To efficiently form the thin film of a high-melting-point material with high adhesive strength by irradiating a material to be treated by the laser light converged on this side of the material, forming the fine particles of the high melting-point material from the raw gas by pyrolysis, and depositing the particles.

CONSTITUTION: A substrate 54 is placed on a substrate holder 52 in a reaction vessel 50. The substrate 54 is irradiated by laser light 66 through an irradiation window 62, and the laser light 66 is converged on a focus 68 on this side of the substrate 54. The raw gas obtained by mixing gaseous SiH_4 and gaseous C_2H_6 is supplied toward the focus 68 through a gaseous mixture nozzle 56. The raw gas is pyrolyzed by the laser light 66 to form fine SiC particles of the high-melting-point material. The formed fine SiC particles are heated by the out-of-focus light, and firmly adhered to the surface of the activated substrate 54 to efficiently form a thin film.